

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 885 648 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

23.12.1998 Bulletin 1998/52

(51) Int. Cl.<sup>6</sup>: B01D 53/86, A62D 3/00

(21) Application number: 98110080.3

(22) Date of filing: 03.06.1998

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 20.06.1997 JP 163717/97

(71) Applicant: Hitachi, Ltd.

Chiyoda-ku, Tokyo 101-8010 (JP)

(72) Inventors:

- Kanno, Shuichi  
Hitachi-shi, Ibaraki 319-1225 (JP)
- Ikeda, Shinzou  
Naka-gun, Ibaraki 319-1114 (JP)

• Yasuda, Ken

Nerima-ku, Tokyo 177-0033 (JP)

• Yamashita, Hisao

Hitachi-shi, Ibaraki 316-0011 (JP)

• Azuhata, Shigeru

Hitachi-shi, Ibaraki 319-1225 (JP)

• Tamata, Shin

Higashiibaraki-gun, Ibaraki 311-1301 (JP)

• Irie, Kazuyoshi

Hitachi-shi, Ibaraki 317-0077 (JP)

(74) Representative:

Strehl Schübel-Hopf & Partner

Maximilianstrasse 54

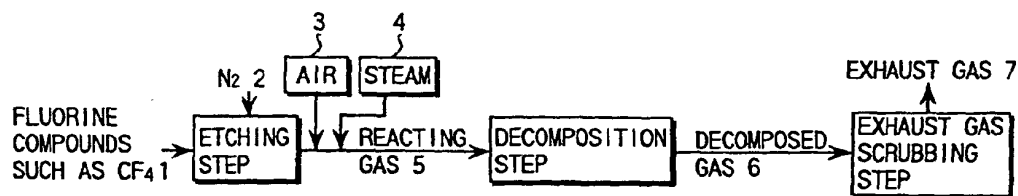
80538 München (DE)

(54) **A treatment method for decomposing fluorine compounds, and catalyst and apparatus therefor**

(57) A method of treatment for decomposing fluorine compounds, comprising the step of contacting a gas flow containing said fluorine compounds, which comprises fluorine as a halogen element, and any of the elements carbon, nitrogen, and sulphur as a compound with said fluorine, with a fluorine compound-decomposi-

tion catalyst in the presence of steam at a temperature in the range of approximately 200 to 800°C to hydrolyse the fluorine compound in said gas flow, wherein said gas flow containing said fluorine compounds is contacted with a catalyst comprising Al to convert said fluorine compounds to hydrogen fluoride.

FIG. 1



EP 0 885 648 A1

The method of treatment for decomposing the fluorine compounds of the present invention uses a catalyst containing Al. The Al is used in a form of an oxide. Al can be used in both alone and as a complex with at least one component selected from the group consisting of Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce, and Si. A decomposing activity of the catalyst can be enhanced by adding S to these catalysts.

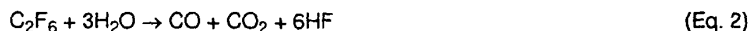
5 Necessary characteristics as catalytic performance are having a high decomposition rate and a long catalytic life. After investigating in detail of the catalyst having the above performance, it was found that a single body composed of only  $\text{Al}_2\text{O}_3$  could have a high decomposition performance depending on its kind of raw material.

A higher decomposition rate can be obtained by using a catalyst, which contains at least one element selected from the group consisting of Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce, and Si in addition to Al, than a case when only Al is used as the catalyst. In these catalyst, Al exists in a form of  $\text{Al}_2\text{O}_3$ , or a complex oxide with the added metallic element. Any of 10 Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, and Si exists in a form of an oxide, or a complex oxide with Al. In accordance with these catalyst, an atomic ratio of Al : M (where, M is at least one of Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, and Si) is desirably in the range of 50 - 99 mol % for Al, and 50 - 1 mol % for M. When the catalyst is composed of Al and Pt, the catalyst desirably contains Pt by 0.1 - 2 % by weight. A high decomposition rate can be obtained by selecting the amount of the additive 15 component other than Al in the range indicated above.

In order to obtain a long catalytic life, suppressing crystallization of the  $\text{Al}_2\text{O}_3$  in the catalyst is effective, and forming a complex oxide of Al such as  $\text{NiAl}_2\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$ , and the like by added metallic components such as Ni, Zr, and the like is desirable. As one of the methods for improving the catalytic performance, a method to add S to the catalyst is known. As a method for adding the S, various methods such as using a sulfuric acid salt, or sulfuric acid, when manufacturing 20 the catalyst can be used. The S in the catalyst exists in a form of  $\text{SO}_4$  ions and the like, and operates to enhance an acidic property of the catalyst. The amount of S is desirably in the range of 0.1 - 20 % by weight.

In accordance with the method of treatment for decomposition of the present invention, oxygen can be added into the gas flow containing the fluorine compound such as  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and the like. The oxygen can be used for an oxidation reaction of CO and the like in the decomposition gas.

25 Representative reactions of the fluorine compound decomposing reaction are as follows:



In accordance with the reactions expressed by the Eq. 1 and Eq. 2, CO is generated. However, the catalyst of the present invention has CO oxidizing performance, and if oxygen exists, CO can be oxidized to  $\text{CO}_2$ .

40 The amount of added steam is required to be controlled so as to generate hydrogen atoms in an amount of at least equivalent to the number of F in the fluorine compound to be treated. Accordingly, fluorine in the compound can be converted to hydrogen fluoride, and a condition which facilitates post-treatment can be generated.

The reaction temperature for hydrolyzing the fluorine compound is desirably in the range of approximately 200 - 800 °C. The range of approximately 500 - 800 °C is desirable as the reaction temperature for treating the fluorine compound, which is composed of at least carbon, fluorine, and hydrogen. If a temperature higher than the above range is used, a 45 higher decomposition rate can be achieved, but rapid deterioration of the catalyst is caused. Furthermore, the corrosion velocity of the apparatus material is increased rapidly. On the contrary, if a temperature lower than the above range is used, the decomposition rate is low.

When contacting the gas flow containing the fluorine compound, which contains only fluorine as the halogen, and any element selected from the group consisting of carbon, sulfur, and nitrogen, with the catalyst of the present invention, 50 the content of the fluorine compound in the gas flow is desirably in the range of 0.1 - 10 % by volume, and preferably 0.1 - 3 % by volume. The space velocity is desirably in the range of 100 per hour - 10,000 per hour, and preferably 100 per hour - 3,000 per hour. Where, the space velocity is defined by the following equation.

$$\text{Space velocity (h}^{-1}\text{)} = \text{Flow rate of the reacting gas (ml/h)} / \text{the amount of catalyst (ml)}$$

55 In accordance with the method of treatment for decomposing fluorine compounds of the present invention, hydrogen fluoride, carbon dioxide, and the others are generated as decomposition products. Additionally, sulfur oxides such as  $\text{SO}_2$ ,  $\text{SO}_3$ , and the like, and nitrogen oxides such as NO,  $\text{NO}_2$ , and the like, are generated in some cases. In order

FIG. 2 is a graph indicating performance of respective of the catalysts of the present invention,  
 FIG. 3 is a graph indicating performance of respective of the catalysts of the present invention,  
 FIG. 4 is a graph indicating performance of respective of the catalysts of the present invention,  
 FIG. 5 is a graph indicating performance of respective of the catalysts of the present invention, and  
 FIG. 6 is a graph indicating performance of respective of the catalysts of the present invention,  
 FIG. 7 is a graph indicating results of decomposition reactions of  $\text{SF}_6$ , and  $\text{C}_3\text{F}_8$ ,  
 FIG. 8 is a graph indicating results of decomposition reactions of  $\text{CF}_4$ ,  $\text{C}_4\text{F}_8$ , and  $\text{CHF}_3$ , and  
 FIG. 9 is a schematic illustration indicating an example of the apparatus for treating fluorine compound of the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention is explained in details with preferred embodiments. The present invention is not restricted to only the embodiments.

FIG. 1 indicates an example of a flow sheet of the treating process for decomposing halogen compounds used in a semiconductor etching process.

In accordance with the etching process, a halogen compound 1 such as  $\text{CF}_4$ , and the like, is charged into a reduced pressure etching chamber, excited with plasma for 20 minutes, and reacted with semiconductors. Subsequently, the atmosphere in the chamber is replaced with  $\text{N}_2$  to dilute the concentration of the halogen compound to a few %, and released as an exhaust gas by a velocity of approximately 10 liter/min.

Air was added by the gas adder 3 to the exhaust gas to dilute the fluorine compound such as  $\text{CF}_4$ , and the like. At this time, nitrogen can be added to dilute the fluorine compound. Furthermore, both nitrogen and oxygen can be added to dilute the fluorine compound. A reacting gas 5, which is obtained by adding steam by the steam adder 4 to the diluted exhaust gas, is transferred to the decomposition step. The decomposition step is performed at the reactor filled with catalyst. The concentration of the fluorine compound in the reacting gas is approximately 0.5 - 1 %.

In the decomposition step, the reacting gas is contacted with a catalyst comprising Al at a temperature in the range of approximately 200 - 800 °C under a condition of space velocity 1,000 per hour ( where, space velocity ( $\text{h}^{-1}$ ) = flow rate of reacting gas (ml/h) /the amount of catalyst (ml) ). In this case, the reacting gas may be heated, or the catalyst may be heated by an electric oven and the like. The decomposed gas 6 is transferred to the exhaust gas scrubbing step. In the exhaust gas scrubbing step, an alkaline solution is sprayed in the decomposed gas 6, and an exhaust gas 7, which is obtained by eliminating acidic components in the decomposed gas, is released to outside the treating system. The decomposition rate of the halogen compound such as  $\text{CF}_4$ , and the like is obtained by analyzing the reacting gas 5 and the exhaust gas 7 with FID (Flame Ionization Detector) gas chromatography, and TCD (Thermal Conductivity Detector) gas chromatography, and calculating mass balances at inlet and outlet of the treating system.

FIG. 9 is a schematic illustration indicating an example of the treating-apparatus of the present invention. The reactor 8 is filled with catalyst 9 comprising Al, and the whole body of the reactor can be heated by the heater 10. At a rear stage of the reactor 8, the exhaust gas scrubber 11 having means for spraying 12 an aqueous alkali solution is provided.

### (Embodiment 1)

The present embodiment is an example of studying the activities of various fluorine compound decomposing catalysts.

Air was added to  $\text{C}_2\text{H}_6$  gas of at least 99 % pure to dilute the gas. Steam was further added to the diluted gas. The steam was obtained by supplying pure water to upper portion of a reactor with a microtube pump by approximately 0.2 ml/min. and gasifying the pure water. The concentration of  $\text{C}_2\text{H}_6$  in reacting gas was approximately 0.5 %. The reacting gas was contacted with a catalyst, which had been heated at a designated temperature from outside the reactor by an electric oven, under a space velocity of 2,000 per hour.

The reactor was a reacting tube made of Inconel, of which inner diameter was 32 mm, having a catalyst layer at the middle portion of the reactor. A thermocouple protecting sheath made of Inconel, of which outer diameter was 3 mm, was provided in the catalyst layer. The decomposition generated gas passed through the catalyst layer was bubbled into a calcium fluoride aqueous solution, and subsequently, released outside the system. The decomposition rate of  $\text{C}_2\text{H}_6$  was calculated from the analytical result of FID gas chromatography and TCD gas chromatography by the following equation (math. 1).

$$\text{Decomposition rate} = 1 - (\text{amount of halogen compound at outlet} / \text{amount of supplied halogen compound}) \times 100 (\%) \quad (\text{math. 1})$$

Hereinafter, methods for preparing respective of catalyst examined in the present embodiment under the above

## Catalyst 7;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 95.43 g of stannic chloride hydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Sn = 91 : 9 (mol%) by an atomic ratio.

## Catalyst 8;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution obtained by diluting 22.2 g of dinitrodiamine Pt (II) nitric acid solution (Pt concentration was 4.5 % by weight) with 200 ml of pure water was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst after finishing the above treatment contained Pt by 0.68 % by weight to 100 % by weight of  $Al_2O_3$ .

## Catalyst 9;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 125.87 g of cobalt nitrate hexahydrate was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Co = 91 : 9 (mol%) by an atomic ratio.

## Catalyst 10;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 76.70 g of zirconyl nitrate dihydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zr = 91 : 9 (mol%) by an atomic ratio.

## Catalyst 11;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 124.62 g of cerium nitrate hexahydrate was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Ce = 91 : 9 (mol%) by an atomic ratio.

## Catalyst 12;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 129.19 g of 20% silica sol was added to 300 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Si = 91 : 9 (mol%) by an atomic ratio.

Results of the examination of the above catalysts 1 - 12 at a reacting temperature of 700 °C are indicated in FIG. 2. The decomposition rates by the catalyst comprising Al and Zn, and the catalyst comprising Al and Ni are significantly higher than others, and the decomposition rate of the catalyst comprising Al and Ti is next high. The reason that the catalyst 3 has a higher activity than the catalyst 4 is supposedly based on the effect of S.

## (Embodiment 3)

The present embodiment is a result of examination on activities of catalysts by preparing catalysts, which were obtained by varying the composition of Al and Zn using the same raw materials of Al and Zn as the catalyst 2 in the embodiment 1, and determining their activities.

## Catalyst 2 - 1;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 215.68 g of zinc nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 80 : 20 (mol%) by an atomic ratio.

## Catalyst 2 - 2;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 369.48 g of zinc nitrate hexahydrate was added to 200 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 70 : 30 (mol%) by an atomic ratio.

## Catalyst 2 - 3;

Commercial boehmite powder was dried at 120 °C for 1 hour. An aqueous solution dissolving 96.39 g of zinc nitrate hexahydrate was added to 126.65 g of the dried powder, and kneaded. After kneading, the mixture was dried at a temperature in the range of 250 - 300°C for approximately 2 hours, and subsequently, calcined at 700 °C for 2 hours. The obtained calcined bodies were pulverized and sieved to obtain granules having a diameter in the range of 0.5 - 1 mm. The granules were used in the examination. The catalyst composition after finishing the above treatment was Al : Zn = 85 : 15 (mol%) by an atomic ratio.

The activities of the above catalysts from the catalyst 2, the catalyst 2 - 1 to the catalyst 2 - 3 were examined by the same method as the embodiment 1 except changing the concentration of  $C_2F_6$  to 2%, and the supplying amount of the pure water to approximately 0.4 ml/min. The decomposition rates at 6 hours elapsed after initiating the examination are indicated in FIG. 4. The highest decomposition rate can be obtained when the mol % of Zn/(Zn+Al) is in the range of 10 - 30 mol %.

## (Embodiment 4)

The present embodiment is a result obtained by performing decomposition of  $CF_4$ ,  $CHF_3$ , and  $C_2F_6$  at various reaction temperatures. The condition of the examination was as same as the embodiment 1, except changing the space velocity to 1,000 per hour, and the halogen compound was diluted with nitrogen instead of air. The catalyst used was the catalyst 4 - 3 in the embodiment 2. The results of the examination at various reacting temperature are indicated in FIG. 5. The catalyst comprising Al and Ni has a high decomposition rate with  $CF_4$ , and  $CHF_3$ . These catalyst also have a high activity with the fluorine compounds at a low temperature such as approximately 600 °C.

## (Embodiment 5)

The present embodiment is a result obtained by examining the effect of steam in the decomposition of  $C_2F_6$ . The condition of the examination was as same as the embodiment 1, except changing only the space velocity to 1,000 per hour. The catalyst used was the catalyst 4 in the embodiment 1, and the reacting temperature was 700 °C. In the examination, steam was supplied for 2 hours from the initiation of the reaction, and then, steam supply was stopped. After 5 hours elapsed, the steam supply was resumed. The results of the examination are indicated in FIG. 6. It was revealed that the decomposition rate was increased by adding steam, and the decomposition of  $C_2F_6$  was performed by hydrolysis.

pound, and said  $\text{NF}_3$  is decomposed to at least either one of NO and  $\text{NO}_2$ , and HF.

5. The method any preceding claim, wherein said gas flow containing said hydrogen fluoride, after contacting with the catalyst, is neutralised by scrubbing with an aqueous alkali solution.

5

6. A catalyst for decomposing fluorine compounds containing an Al oxide, which is used for hydrolysing halogen compounds containing only fluorine as the halogen.

7. The method of any of claims 1 to 5 or the catalyst of claim 6, wherein said catalyst contains Al, at least one of the elements Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, Si, and Pt, the atomic ratio of Al : M (where, M is any one of Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce and Si) being preferably 50 to 99 mol % for Al and 50 to 1 mol % for M.

10

8. The method or catalyst of claim 7, wherein said catalyst further contains S, preferably in the range of 0.1 to 20 % by weight.

15

9. The method or catalyst of claim 7 or 8, wherein respective of components comprising said catalyst is contained in any form of an oxide of the component alone, and a complex oxide of Al with other components.

10. The method or catalyst of any of claims 7 to 9, wherein said catalyst contains Al and 0.1 to 2 % by weight of Pt.

20

11. A treating apparatus for decomposing fluorine compounds comprising

a reactor filled with catalyst for decomposing fluorine compounds,  
a gas adder to generate a gas flow containing a compound, which is composed of fluorine and any one of carbon, sulphur, and nitrogen, by adding any of nitrogen, oxygen, and air to said fluorine compounds, which is introduced into said reactor,  
a heater for heating at least any one of said catalyst filled in said reactor and said gas flow supplied to said reactor to a temperature in the range of approximately 200 to 800 °C, and  
a steam adder for adding steam for hydrolysing said fluorine compounds to said gas flow,  
wherein said reactor is filled with a catalyst comprising Al.

25

30

12. The apparatus of claim 11, wherein an exhaust gas scrubber for scrubbing said gas flow discharged from said reactor with an aqueous alkali solution is provided at a rear stage of said reactor.

35

40

45

50

55

FIG.3

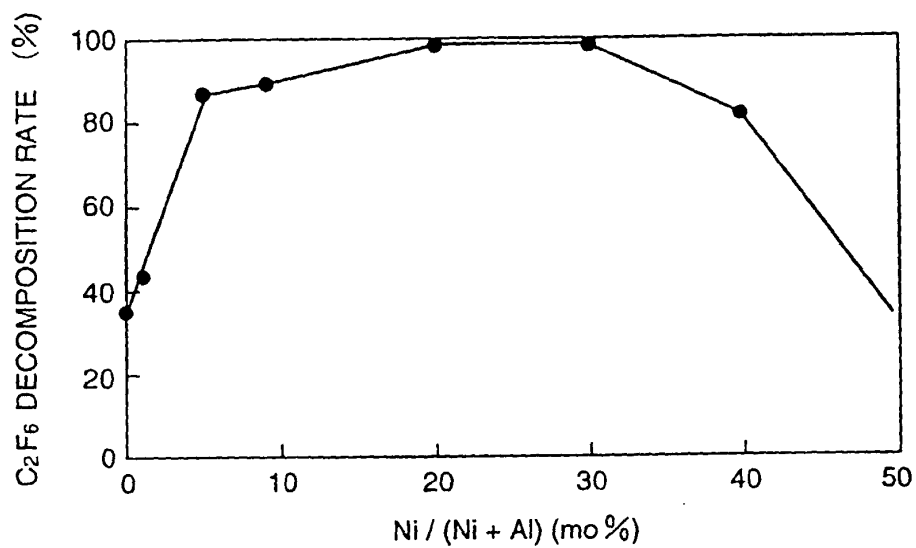


FIG.4

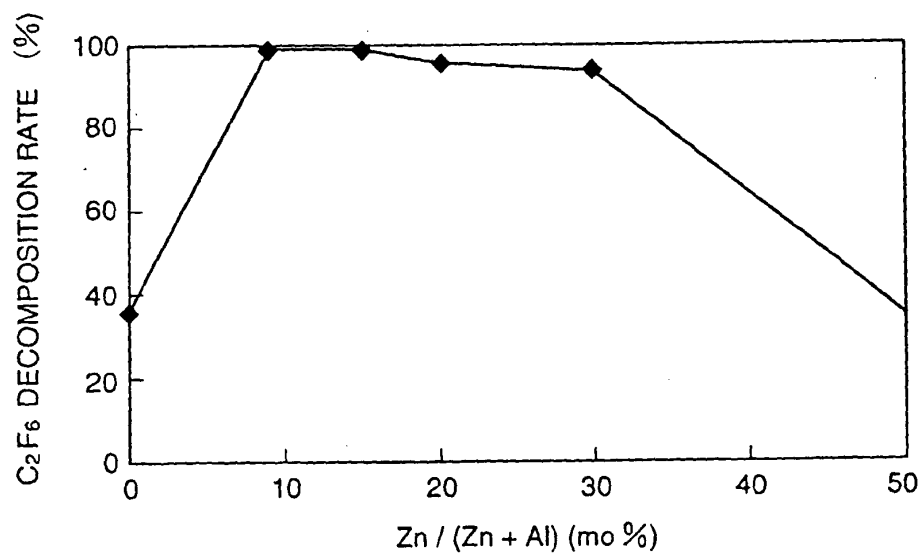


FIG.7

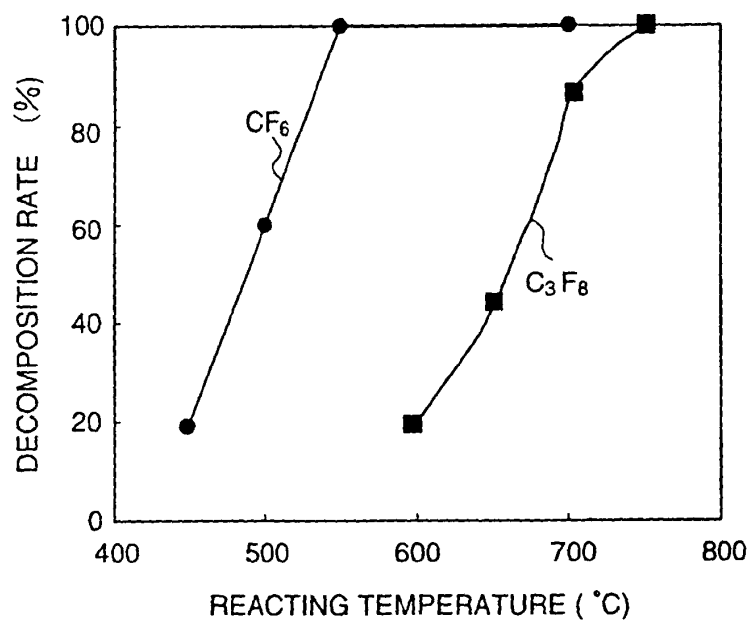
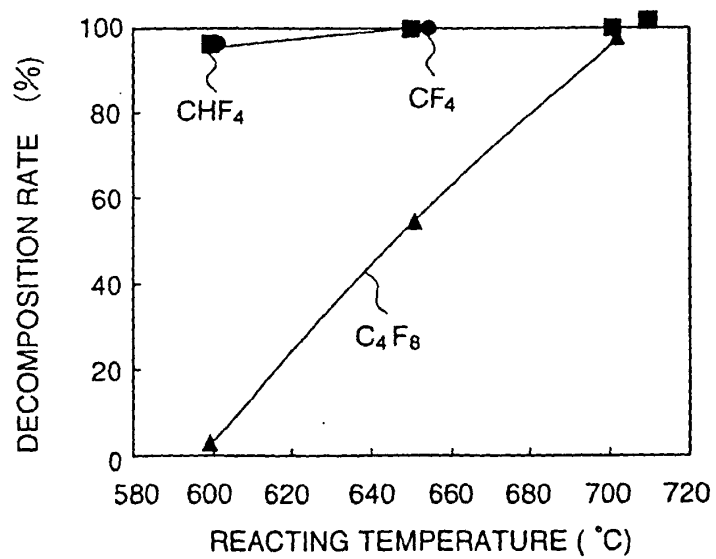


FIG.8







European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 0080

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	WO 97 49479 A (CS HALBLEITER SOLARTECH ) 31 December 1997 * page 4, paragraph 1 - page 5, paragraph 1 * * page 7, paragraph 2 - paragraph 4 * * page 9, paragraph 1 * * page 14, paragraph 3 * ---	1-4,6,7, 9	B01D53/86 A62D3/00
X	EP 0 642 809 A (CHEMIE LINZ GMBH) 15 March 1995 * page 1, line 27 - page 51 * * page 2, line 28 - line 57; example 1 * ---	1,2,5-7, 9,11,12	
X	DE 43 11 061 A (SOLVAY FLUOR & DERIVATE) 6 October 1994 * the whole document * ---	1,4,6	
X	DATABASE WPI Section Ch, Week 8802 Derwent Publications Ltd., London, GB; Class E36, AN 88-010405 XP002078730 & JP 62 273 039 A (KANTO DENKA KOGYO KK) * abstract * ---	1,4,6,7	TECHNICAL FIELDS SEARCHED (Int.Cl.6)  B01D A62D
X	EP 0 597 393 A (JAPAN PIONICS) 18 May 1994 * claims; table 7 * ---	1,4,6,7	
X,D	EP 0 412 456 A (MITSUI DU PONT FLUORCHEMICAL) 13 February 1991 * page 3, line 12 - page 4, line 37; examples * -----	1,5-7,9, 11,12	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 25 September 1998	Examiner Eijkenboom, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (P04/C01)